Potential Applications of ALFF in Cosmochemistry and Geochemistry

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There are many unique opportunities for research in cosmochemistry and geochemistry that take advantage of the combination of brightness, tunability and access to short wavelengths. For many of these, the SPIRIT end-station is an essential part of the measurements. The applications outlined here represent only a few of those possible, limited by the interests and expertise of those attending the workshop on October 30 and 31.

1. Resonant-ionization mass spectrometry (RIMS) of carbon, nitrogen, oxygen, and noble-gas isotopes in special samples.

In a very successful collaboration between the Argonne National Laboratory and the University of Chicago, the RIMS technique has been developed for isotopic analysis of metallic elements in "stardust": micrometer-sized mineral grains extracted from meteorites. These grains are found in the expanding or exploding envelopes of stars that preceded our own Sun, and carry the isotopic record of nuclear processes occurring in their parent stars. The RIMS technique involves a multi-photon photoionization of atoms that have been sputtered or ablated from a sample surface. For metallic elements, such as Ca, Ti, Fe, Sr, Zr, Mo, and Ba (which have been studied), the necessary resonant photons are in the energy range accessible by conventional lasers. For the non-metallic elements, C, N, O, Ne, the energy required for the initial excitation step is in the range 7–12 electron-volts, which is beyond the range of tunable conventional lasers, but which will be readily attainable by ALFF.

One of the most important potential applications of RIMS to isotopic analysis of small quantities of C, N, and O is in the measurement of the isotopic composition of the solar wind. The Genesis spacecraft is currently orbiting the L1 La Grange point between the Sun and Earth, collecting implanted solar win ions in specially selected and prepared solid surfaces (of silicon, gold, and diamond). Analytical techniques for isotopic analysis of these precious samples are under development, but will not be ready when the sample is returned to Earth in 2004. A RIMS measurement using selective multi-photon ionization by ALFF, and isotopic analysis by SPIRIT has all of the needed characteristics to provide the prescribed accuracy of isotope ratio measurements (one part per thousand) for carbon, nitrogen, and oxygen, which are the first priority of the Genesis mission.

Other cosmochemical applications that require the combined capabilities of ALFF and SPIRIT include the following: (1) neon isotopes in Genesis samples, which are being collected on different surfaces for the different energy regimes of the solar wind; (2) oxygen isotopes in iron meteorites, essential for establishing genetic relations between iron meteorites and stony meteorites, and thus for understanding the formation of iron cores in asteroids and planets; (3) microscopic distribution of nitrogen isotopes in iron meteorites, for which bulk analyses show wide, unexplained variations; (4) nitrogen isotopes in minerals from the Earth's mantle, which is probably the principal reservoir for nitrogen on Earth (although at a concentration of about one part per million by mass); the result is necessary both for the degassing history of the Earth and for identifying the origin of essential volatile elements (H, C, N) on Earth.

2. Single-photon ionization of geochemical and cosmochemical elements and compounds.

Geochemists have long sought an analytical technique that would provide simultaneous quantitative analysis of all elements in a rock or mineral. The first approach to this goal was emission spectroscopy, in which a sample is excited by an electric arc, and a visible-light spectrum is recorded on a photographic plate. This was the dominant technique in the 1920's–40's, but has limited accuracy, and requires internal standardization. A successor technique was spark-source mass spectrometry, in which ions produced in the spark discharge are measured mass spectrometrically. However, ionization efficiencies vary widely from one element to another, again requiring internal standards. Secondary-ion mass spectrometry (SIMS) is a useful variant for microanalysis, in which sample ions are produced by bombardment by a focussed primary ion beam. However, SIMS has limited sensitivity, and produces mass spectra that are made very complicated due to the presence of molecular ions, which may "interfere with" the atomic ions of interest. It is hoped that non-selective photoionization might provide a new analytical technique that is both highly sensitive for all elements and also capable of producing simple mass spectra. Photoionization provides greater sensitivity than any existing microbeam technique.

Preliminary experiments at Argonne National Laboratory have been carried out with a fluorine laser (monochromatic light at 157 nm), and have not shown the desired uniformity of sensitivity across a broad range of elements. The tunability and wider range of available photon energies of ALFF may improve the usefulness of this technique.

If the ALFF-SPIRIT combination proves satisfactory for trace-element analysis, the appropriate applications will be those for which small sample size is the limitation. These include:

(1) presolar "stardust" grains, with dimensions on the order of one micrometer, and element abundance on the order of one ppm;

(2) cometary dust particles, such as those to be returned to Earth by NASA's "Stardust" mission, with sub-micrometer dimensions and unknown elemental abundances;

(3) meteorites or geologic materials in which micrometer-scale spatial resolution is important;

(4) samples from experimental petrology, especially those from very-high-pressure diamond anvil cells, which are necessarily very small.

3. Organic molecular analysis.

In both terrestrial and extraterrestrial natural materials, there is a great need for identification and quantification of organic molecules, both biogenic and abiogenic. In meteorites, particularly in carbonaceous chondrites, there is a great need to identify the level of complexity and variety achievable in natural, abiogenic processes. In ancient terrestrial rocks, chemical or isotopic signatures of biological processes are often ambiguous, so that even less diagnostic features, such as morphology, are called upon. New, microbeam techniques are required for excitation and detection of organic molecular species, with minimal fragmentation. The ALFF radiation is in the appropriate energy range for single-photon ionization, and its tunability is an invaluable asset in allowing molecular identification by tuning above and below specific ionization thresholds.

4. Astronomical applications.

The understanding of chemical processes in the interstellar medium and in molecular clouds depends fundamentally on knowledge of the abundances of the major reactive elements, particularly hydrogen, carbon, nitrogen, and oxygen. The techniques for determining these abundances depend on the absorption of ultraviolet light from background stellar sources. These elements are so abundant that allowed electronic transitions are optically thick, and are, therefore, not very useful for accurate abundance determinations. Electronic transitions are known for the key species: C^+ ions, N atoms, and O atoms, for which the *f*-values (transition probabilities) are low enough that the lines are ideal for quantitative analysis. However, the very fact that the *f*-values are small makes them difficult to measure experimentally. The great enhancement in brightness of ALFF, relative to third-generation synchrotron radiation, makes it possible to determine these crucial *f*-values.